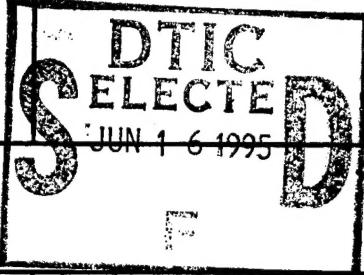


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REPORT DOCUMENTATION PAGEForm Approved
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 10 June 1995	3. REPORT TYPE AND DATES COVERED Technical	
4. TITLE AND SUBTITLE The First Example of an Aluminum-Phosphorus-Arsenic Mixed-Pnicogen Ring Compound: $\text{Et}_2\text{AlP}(\text{SiMe}_3)_2\text{Al}(\text{Et})_2\text{As}(\text{SiMe}_3)_2$		5. FUNDING NUMBERS •N00014-89-J-1545 R&T Project 3135008--14 •N00014-95-1-0194 R&T Project 3135008--16 •N00014-93-1-0860 R&T Project 4135008--13 •Dr. Harold E. Guard	
6. AUTHOR(S) Janeen A. Laske Cooke, Richard L. Wells* and Peter S. White		8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report No. DU/DC/TR-50//AASERT-02	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Duke University Durham, NC 27708-0346		9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 300 North Quincy Street Arlington, VA 22217-5000	
10. SPONSORING / MONITORING AGENCY REPORT NUMBER 		11. SUPPLEMENTARY NOTES Accepted for Publication in <i>Organometallics</i>	
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for Public Release Distribution Unlimited		12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The aluminum mixed-pnicogen compound $\text{Et}_2\text{AlP}(\text{SiMe}_3)_2\text{Al}(\text{Et})_2\text{As}(\text{SiMe}_3)_2$ (1) is the first structurally-characterized compound to contain a four membered ring with two aluminum centers bridged by two different heavier group 15 atoms. Compound 1 was synthesized by the eqilibration of $[\text{Et}_2\text{AlP}(\text{SiMe}_3)_2]_2$ (2) and $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$ (3) in a 1:1 mole ratio under ultrasonic conditions. Low-temperature X-ray crystalslographic analysis revealed that crystals of 1 belong to the monoclinic system, space group $C2/c$ (C_2h^6), with unit cell dimensions of $a = 17.960(4)$, $b = 9.328(1)$, $c = 20.194(5)$ Å, and $\beta = 100.33(2)^\circ$ for $Z = 4$, and isomorphous with those of 2 and 3 . The electron ionization (20 ev) mass spectrum of 1 shows a fragmentation pattern consistent with this compound and no peaks above m/z 400 consistent with either 2 or 3 .			
DTIC QUALITY IMPROVED 3			
14. SUBJECT TERMS Aluminum, Phosphorus, Arsenic, Four-membered Ring Synthesis, Crystal Structure		15. NUMBER OF PAGES 17	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited

OFFICE OF NAVAL RESEARCH

Grant N00014-89-J-1545
R&T Project 3135008---14
and
Grant N00014-95-1-0194
R&T Project 3135008---16
and
Grant N00014-93-1-0860
R&T Project 4135008---13

Dr. Harold E. Guard

Technical Report No. DU/DC/TR-50//AASERT-02

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Janeen A. Laske Cooke, Richard L. Wells and Peter S. White

Accepted for Publication in *Organometallics*

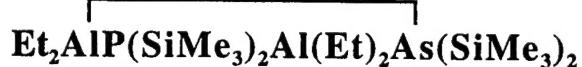
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10 June 1995

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The First Example of an Aluminum-Phosphorus-Arsenic Mixed-Pnicogen Ring Compound: X-Ray Crystal Structure of



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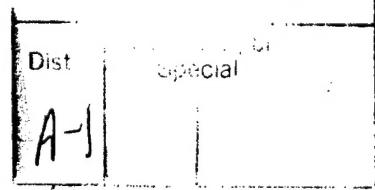
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(Revised May 6, 1995)

Summary: The aluminum mixed-pnicogen compound, $\overbrace{\text{Et}_2\text{AlP}(\text{SiMe}_3)_2\text{Al}(\text{Et})_2\text{As}(\text{SiMe}_3)_2}^{\text{1}}$, is the first structurally-characterized compound to contain a four-membered ring with two aluminum centers bridged by two different heavier group 15 atoms. Compound **1** was synthesized by the equilibration of $[\text{Et}_2\text{AlP}(\text{SiMe}_3)_2]_2$ (**2**) and $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$ (**3**) in a 1:1 mole ratio under ultrasonic conditions. Low-temperature X-ray crystallographic analysis revealed that crystals of **1** belong to the monoclinic system, space group $C2/c$ (C_{2h}^6), with unit cell dimensions of $a = 17.960(4)$ Å, $b = 9.328(1)$ Å, $c = 20.194(5)$ Å, and $\beta = 100.33(2)$ ° for $Z = 4$, and are isomorphous with those of **2** and **3**. The electron ionization (20 eV) mass spectrum of **1** shows a

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fragmentation pattern consistent with this compound and no peaks above m/z 400 consistent with either **2** or **3**.

Introduction

Much of the research in our laboratory during the past decade has focused on the fabrication of potential single-source precursors to group 13-15 binary semiconductor and electronic materials. Through various synthetic routes, we have been able to isolate several noteworthy oligomeric, monomeric, and Lewis acid-base adduct compounds with novel compositions and structural characteristics.¹⁻¹¹ As an extension of this work, we have been investigating the preparation of compounds containing a group 13 metal and two different pnicogens, which might serve as single-source precursors to ternary 13-15 materials. Our initial efforts to synthesize such metal-pnicogen compounds involved attempted reactions of "mixed-

bridge" binary 13-15 compounds having $\overbrace{M-E-M-Cl}$ ($M = In$ or Ga , $E = P$, As) ring cores with the lithium salts of silylarsines and phosphines, and resulted in unusual binary rearrangement products rather than preferred mixed-pnicogen compounds.¹²

As alternatives to the salt-elimination synthetic pathway, equilibration reactions of analogous group 13-15 dimeric compounds were explored and found to be successful methods of preparing ternary metal-pnicogen compounds. We have recently reported the isolation and

structural characterization of $(Me_3SiCH_2)_2InAs(SiMe_3)_2In(CH_2SiMe_3)_2P(SiMe_3)_2$ (**4**)¹³ and

$I_2GaAs(SiMe_3)_2Ga(I)_2P(SiMe_3)_2$ (**5**),¹⁴ which are the first examples of four-membered ring compounds containing two group 13 metal centers bridged by both an arsenic and a phosphorus atom. Both **4** and **5** were prepared by the equilibration of equimolar amounts of two isostructural dimers of the formulae $[(Me_3SiCH_2)_2InE(SiMe_3)_2]_2$ [$E = As$ (**6**)¹⁵ and P (**7**)³] and $[I_2GaE(SiMe_3)_2]_2$ [$E = As$ (**8**)¹⁶ and P (**9**)¹⁴], respectively. These results led us to equilibrate two

analogous organoaluminum dimeric compounds in a similar fashion in an effort to isolate an Al-P-As mixed-pnictogen product. To this end, the previously reported dimers, $[\text{Et}_2\text{AlP}(\text{SiMe}_3)_2]_2$ (**2**)⁸ and $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$ (**3**)², were equilibrated in a 1:1 mole ratio under ultrasonic conditions, forming the ring compound **1**. Herein, we describe the synthesis and structural characterization of the aluminum mixed-group 15 compound, $\overbrace{\text{Et}_2\text{AlP}(\text{SiMe}_3)_2\text{Al}(\text{Et})_2\text{As}(\text{SiMe}_3)_2}^{\text{1}}$ (**1**).

Experimental Section

General Considerations. All manipulations were performed by Schlenk techniques or in a Vacuum Atmospheres HE-493 Dri-Lab under argon. Pentane was dried over LiAlH_4 and distilled under dry nitrogen prior to use. Benzene- d_6 was distilled from sodium/benzophenone under dry nitrogen and toluene- d_8 was used as received from Aldrich Chemical Co., Milwaukee, Wisconsin. Sonication of reaction solutions was performed in a L&R Ultrasonics Quatrex 140H ultrasonic cleaning bath. Compounds **2**⁸ and **3**² were prepared by literature methods.

^1H , ^{27}Al , and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were acquired on a Varian Unity 500 (500.1, 130.3, and 202.4 MHz, respectively) spectrometer using 5-mm tubes. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained on a Varian XL-300 (75.4 MHz) spectrometer also using 5-mm tubes. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to TMS *via* the residual protons or carbons of benzene- d_6 at δ 7.15 or 128.0 ppm. ^{27}Al and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were externally referenced to $\text{Al}(\text{NO}_3)_3$ and H_3PO_4 , respectively, at δ 0.00 ppm. Melting Points (uncorrected) were taken in flame-sealed capillaries on a Thomas-Hoover Uni-melt apparatus. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, New York. Single crystal data for **1** were collected at the University of North Carolina - Chapel Hill on a Rigaku AFC6/S diffractometer at -130°C, with graphite-monochromated $\text{Mo}-K_\alpha$ radiation.

Preparation of $\text{Et}_2\text{AlP}(\text{SiMe}_3)_2\text{Al}(\text{Et})_2\text{As}(\text{SiMe}_3)_2$ (1). A one-necked screw-top round-bottomed flask, equipped with a Teflon valve and stir-bar, was charged with 0.262 g (0.499 mmol) of **2** in 30 mL of pentane and 0.306 g (0.499 mmol) of **3** in 30 mL of pentane. The solution was sonicated at 45 °C in an ultrasonic cleaning bath for 24 h, resulting in a clear, colorless solution. The volatiles were removed *in vacuo* leaving a white crystalline solid, which was dissolved in pentane and cooled to -20 °C. After 3 d, colorless X-ray quality single crystals of **1** were isolated (0.527 g, 92.6% yield), mp 261-264.5 °C (Changes from crystalline to glassy, then melts to a colorless liquid). Anal. Calcd. (Found) for $\text{C}_{20}\text{H}_{56}\text{Al}_2\text{AsPSi}_4$: C, 42.23 (41.91); H, 9.92 (10.29); Al, 9.49 (9.10); P, 5.44 (5.66). ^1H NMR (C_6D_6): δ 0.37 [d, 18 H, Me_3SiP ($J_{\text{P}-\text{H}} = 4.7$ Hz)], δ 0.42 (s, 18 H, Me_3SiAs), δ 0.49 (q, 8 H, CH_2), δ 1.37 (m, 12 H, CH_3). $^{13}\text{C}\{\text{H}\}$ NMR: δ 4.38 (s, CH_2), δ 4.46 (s, Me_3SiAs), δ 4.67 [d, Me_3SiP ($J_{\text{P}-\text{C}} = 4.0$ Hz)], δ 9.63 (m, CH_3). ^{27}Al NMR: d 214.05 (br s). $^{31}\text{P}\{\text{H}\}$ NMR: δ -240.93 (s), δ -245.83 (s). The electron ionization (20 eV) mass spectrum shows a peak for $(\text{C}_{18}\text{H}_{51}\text{Al}_2\text{AsPSi}_4)^+$ at m/z 539.2, for $(\text{C}_{17}\text{H}_{47}\text{Al}_2\text{AsPSi}_3)^+$ at m/z 495.2, for $(\text{C}_{14}\text{H}_{41}\text{Al}_2\text{AsPSi}_4)^+$ at m/z 481.2, for $(\text{C}_{14}\text{H}_{38}\text{Al}_2\text{AsSi}_2)^+$ at m/z 391.1, and for $(\text{C}_{14}\text{H}_{38}\text{Al}_2\text{PSi}_2)^+$ at m/z 347.2. These ions correspond to the fragmentation due to the elimination of an ethyl group, the elimination of a single trimethylsilyl group, the elimination of three ethyl groups, the elimination of $\text{P}(\text{SiMe}_3)_2$, and the elimination of $\text{As}(\text{SiMe}_3)_2$ from **1**, respectively.

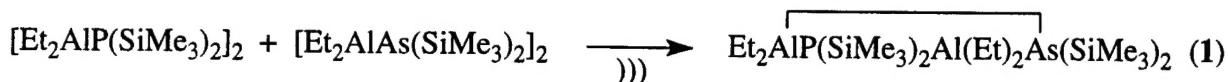
Low Temperature ^1H NMR Study of 1. In a dry box, solid **1** (16.2 mg, 0.0248 mmol) was added to an NMR tube, which was sealed with a septum. 0.7 mL of toluene- d_8 was added to the NMR tube *via* syringe. The tube was placed in the 500 MHz NMR probe, and ^1H NMR spectra were recorded from 25 °C to -42 °C at 20 °C increments, allowing 10 min for equilibration at each temperature. The compound readily dissolved at temperatures above -40 °C, allowing for the acquisition of suitable spectra. At -42 °C, colorless crystals of **1** began to grow out

of solution, preventing further data acquisition at lower temperatures. ^1H NMR (-35 °C): δ 0.37 [d, 18 H, Me_3SiP ($J_{\text{P}-\text{H}} = 4.5$ Hz)], δ 0.42 (s, 18 H, Me_3SiAs), δ 0.52 (q, 8 H, CH_2), δ 1.41 (m, 12 H, CH_3).

X-Ray Structural Analysis of **1.** Crystallographic data and measurements for **1** are summarized in Table 1. A single colorless crystal of **1** was affixed to the end of a glass fiber using a viscous oil under an inert nitrogen atmosphere, then transferred to a goniometer head and cooled to -130 °C under a nitrogen flow. X-Ray intensity data were recorded using the ω scan mode (Mo- K_{α} radiation, $\lambda = 0.71073$ Å). Cell parameters and an orientation matrix corresponded to a monoclinic cell, space group $C\ 2/c$ for **1**. The structure of **1** was solved by direct methods and the refined unit-cell parameters were derived from the diffractometer setting angles for 51 reflections ($40^\circ < 2\theta < 50^\circ$). Intensity data were corrected for absorption using ψ -scans. Positional and thermal parameters were refined using least-squares adjustment techniques; the last least-squares cycle was calculated with 42 atoms, 128 parameters, and 2178 [with $I > 2.5\sigma(I)$] out of the 2909 reflections. In the final iterations, hydrogen atoms were incorporated at their calculated positions using a riding model, with parameter refinement converging at $R = 0.030$ ($R_w = 0.037$). An ORTEP¹⁷ diagram showing the solid-state structure and atom labeling scheme of **1** is shown in Figure 1. Neutral atom scattering factors and their anomalous dispersion corrections were taken from ref 18.

Results and Discussion

The equilibration reaction of $[\text{Et}_2\text{AlP}(\text{SiMe}_3)_2]_2$ (**2**)⁸ and $[\text{Et}_2\text{AlAs}(\text{SiMe}_3)_2]_2$ (**3**)² was carried out in a 1:1 mole ratio in pentane, under ultrasonic conditions at 45 °C, and afforded a white crystalline solid, which was recrystallized from pentane and determined to be the aluminum-mixed-pnictogen compound **1** (eq 1). A crystallographic study of **1** reveals that it is isomorphous with the



isostructural compounds **2**⁸ and **3**². Compound **1** lies on a crystallographic C_2 axis of symmetry and contains a planar, four-membered Al—E—Al—E ring (E = P/As). The unit cell parameters of **1** are all slightly smaller than those of **2** and **3**, rather than being the averages of the starting dimers, which was the case with the indium mixed-pnicogen compound, **4**. Consistent with compounds **4** and **5**, the pnicogen sites in **1** exhibit a 50:50 occupancy ratio for phosphorus and arsenic. The exact identification of the individual pnicogen sites in **1** as P or As is indeterminable by means of X-ray crystallographic analysis, leaving the possibility that crystals of **1** either contain discrete mixed-pnicogen molecules or co-crystallized starting materials, **2** and **3**.

To our knowledge, compound **1** is the first structurally-characterized aluminum mixed-pnicogen ring compound containing two Al centers bridged by two different heavier group 15 atoms. Previously, Schmidbaur and co-workers reported the structure of an aluminum mixed-pnicogen species, but it was an aluminum-nitrogen-phosphorus compound, $\{(\text{CH}_3)_2\text{Al}[\text{P}(\text{C}_6\text{H}_5)_2]\text{N}[\text{P}(\text{C}_6\text{H}_5)_2]\}_2$, containing a six-membered Al-N-P-Al-N-P ring in a twist-conformation.¹⁹ Cowley *et al.* have also reported the syntheses of two compounds containing ternary aluminum core rings; however, they were mixed-metal dimers of the type $\text{Me}_2\text{ME}(\text{tBu})_2\text{M}'(\text{Me})_2\text{E}(\text{tBu})_2$ (M, M' = Al, Ga; E = P, As) and no structural information was provided.²⁰

Crystallographic data and data collection parameters for **1** are summarized in Table 1. An ORTEP¹⁷ diagram showing the solid-state conformation and atom-numbering scheme is presented in Figure 1. Table 2 lists the non-hydrogen atom fractional coordinates and equivalent isotropic thermal parameters with estimated standard deviations. Selected bond lengths and bond angles are provided in Table 3.

Compound **1** crystallizes in the monoclinic space group $C2/c$ (C_{2h}^6) and has a unit cell with four discrete molecules lying on crystallographic centers of symmetry. The pnicogen-aluminum

bonds lengths of 2.499(1) Å and 2.494(1) Å in **1** are the averages of the Al—P bonds in **2** [2.460(1) and 2.454(1) Å] and the Al—As bonds in **3** [2.539(1) and 2.531(1) Å], respectively. Such similarities were previously observed when the In—As/P bond lengths of **4** were compared to those of the In—As and In—P bonds in **6** and **7**. The Al and the pnicogen centers in **1** reside in pseudotetrahedral environments. The Al—As/P—Al(a) angles in **1** are 90.44(3)° and are slightly larger than the As/P—Al—As/P(a) angles of 89.56(3)°, an effect also observed in the indium mixed-pnicogen ring of **4**, and similar 13-15 four-membered ring systems^{3,23}. The exocyclic angles at the pnicogen and aluminum centers in **1**, Si(1)—As/P—Si(2) [107.90(3)°] and C(1)—Al—C(3) [114.8(1)°], are nearly identical to the averages of the corresponding angles in **2** and **3** (107.8° and 114.6°).

Electron ionization mass spectroscopy (20 eV) was used to investigate the gas-phase behavior of **1** as additional evidence of the proposed crystal structure. Although a peak for the molecular ion (M^+) was not observed, the mass spectrum of **1** shows an ion peak at m/z 539.2, arising from the loss of an ethyl group, and at m/z 495.2 due to the loss of a (Me_3Si) group from the parent ion. A peak at m/z 481.2 can be attributed to the ($M - Et_3$)⁺ ion. The noted presence of single gas-phase ions containing aluminum, arsenic, and phosphorus in the mass spectrum of **1** supports the results of the crystallographic analysis. No peaks corresponding to molecular ions of **2** (m/z for $M^+ = 524.9$) or **3** (m/z for $M^+ = 613.0$) were observed above m/z 400 in the mass spectrum. Melting point studies revealed a melting range of 261-264.5 °C for crystals of **1**, which is unique from those of the equilibrated dimers, **2** (280-282.5 °C) and **3** (201 °C). If compound **1** was composed of co-crystallized starting materials, one would expect a broad melting point range rather than the observed range of 3.5 °C.

Solution ¹H, ¹³C, ²⁷Al, and ³¹P NMR spectra are consistent with the solid-state structure of **1** described in Figure 1. The room temperature ¹H NMR spectrum of **1** is unique from those of the starting materials, **2** and **3**. The protons of the Me_3Si groups on the phosphorus and arsenic atoms give rise to a doublet at δ 0.37 ppm and a singlet at δ 0.42 ppm, respectively. Notably absent is the triplet which would be expected if the core ring of **1** contained two chemically-

equivalent P atoms, as does dimer **2**. The ^{13}C NMR spectrum of **1** also exhibits a doublet at δ 4.67 arising from the carbons in the phosphorus trimethylsilyl groups, indicating the presence of only one P center in the ring. A solution ^{27}Al NMR study of **1** showed a broad signal at δ 214.05 ppm, which is significantly shifted from the ^{27}Al signals for **2** and **3** (δ 164.3 and δ 187.87 ppm, respectively), but is still well-within the expected ppm range for a four-coordinate tetrahedral Al center

Two peaks are present in the ^{31}P NMR spectrum of **1**: a singlet at δ -240.93 ppm and a slightly smaller singlet at δ -245.83 ppm. The lone phosphorus nucleus in the Al-P-Al-As ring of **1** gives rise to the primary singlet at δ -240.93 ppm. The smaller peak at δ -245.83 ppm corresponds to a minor signal (δ -245.10 ppm) observed in a ^{31}P solution spectrum of **2**, which was obtained upon long-standing of an NMR sample of **2**. This upfield signal may be attributed to the presence of the $\text{Et}_2\text{AlP}(\text{SiMe}_3)_2$ moiety, which is generated by the dissociation of the core rings of both **1** and **2** in solution to form monomeric species. The ^{31}P NMR spectral features of **1** correspond to those of the spectra for the mixed-pnicogen compounds, **4** and **5**, as do those of the ^1H and ^{13}C NMR spectra. Low-temperature ^1H NMR experiments were performed in order to investigate the possibility of dynamic behavior of compound **1**, but proved inconclusive. No changes in peak shape or area were observed between 25 °C and -35 °C. However, further cooling caused a broadening of all ^1H signals due to the recrystallization of the compound.

Conclusions

As demonstrated by the work reported herein, equilibration reactions between dimeric analogs, containing the same group 13 metal but different pnicogen atoms, can be used as synthetic routes to mixed-pnicogen compounds. Compound **1** is the first example of a ring containing two

aluminum centers bridged by two different heavier group-15 elements - phosphorus and arsenic. Currently, our laboratory is studying the use of equilibration reactions to prepare other examples of mixed-pnicogen and mixed-metal 13-15 compounds. The potential for these classes of compounds to act as single-source precursors to group 13-15 ternary electronic materials is also being investigated.

Acknowledgment: We are grateful for the financial support of this work provided by the Office of Naval Research - AASERT Program. The National Science Foundation (Grant 9116161) and the North Carolina Biotechnology Center (Grant 9210-IDG-1008) are gratefully acknowledged for their financial support for the mass spectrometer. We also thank Dr. George R. Dubay and Dr. James Kenar of the P. M. Gross Chemical Laboratory at Duke University for performing the electron ionization mass spectroscopy of our compounds, and Dr. Anthony A. Ribeiro of the Duke NMR Spectroscopy Center for assisting with the NMR studies of the title compound.

Supplementary Material Available: Tables of non-hydrogen and hydrogen atom coordinates and isotropic thermal parameters, anisotropic temperature factors, and all interatomic bond distances and bond angles for **1**. Ordering information is given on any current masthead page.

References

- (1) Wells, R. L. *Coord. Chem. Rev.* **1992**, *112*, 273-291.
- (2) Wells, R. L.; McPhail, A. T.; Speer, T. M. *Organometallics* **1992**, *11*, 960.
- (3) Wells, R. L.; McPhail, A. T.; Self, M. F. *Organometallics* **1992**, *11*, 221.
- (4) Wells, R. L.; McPhail, A. T.; Jones, L. J., III; Self, M. F.; Butcher, R. J. *Organometallics* **1992**, *11*, 2694.
- (5) Wells, R. L.; Aubuchon, S. R.; Self, M. F.; Jasinski, J. P.; Woudenberg, R. C.; Butcher, R. J. *Organometallics* **1992**, *11*, 3370.
- (6) Wells, R. L.; McPhail, A. T.; Jones, L. J., III; Self, M. F. *J. Organomet. Chem.* **1993**, *449*, 85.
- (7) Wells, R. L.; Self, M. F.; McPhail, A. T.; Aubuchon, S. R.; Woudenberg, R. C.; Jasinski, J. P. *Organometallics* **1993**, *12*, 2832.
- (8) Wells, R. L.; McPhail, A. T.; Self, M. F.; Laske, J. A. *Organometallics* **1993**, *12*, 3333.
- (9) Wells, R. L.; Self, M. F.; Baldwin, R. A.; White, P. S. *J. Coord. Chem.* **1994**, *33*, 279.
- (10) Wells, R. L.; Baldwin, R. A.; White, P. S. *Organometallics*, In Press.
- (11) Wells, R. L.; McPhail, A. T.; Laske, J. A.; White, P. S. *Polyhedron* **1994**, *13*, 2737.
- (12) Wells, R. L.; McPhail, A. T.; Jones, L. J.; Self, M. F. *Organometallics* **1992**, *11*, 2694.
- (13) Jones III, L. J.; McPhail, A. T.; Wells, R. L. *Organometallics* **1994**, *13*, 2504.
- (14) Wells, R. L.; Aubuchon, S. R.; Lube, M. S.; White, P. S. *Main Group Chem.*, In Press.
- (15) Wells, R. L.; Jones, L. J.; McPhail, A. T.; Alvanipour, A. *Organometallics* **1991**, *10*, 2345.
- (16) Johansen, J. D.; McPhail, A. T.; Wells, R. L. *Adv. Mater. Opt. Electron.* **1992**, *1*, 29.
- (17) Johnson, C. K. "ORTEP - A Fortran Thermal Ellipsoid Plot Program," ONRL-5138, Oak Ridge National Laboratory, **1976**.
- (18) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, **1974**; Vol. IV (present distributor, D. Reidel, Dordrecht).
- (19) Schmidbaur, H.; Lauteschlager, S.; Milewski-Mahrta, B. *Chem. Ber.* **1983**, *116*, 1403.
- (20) Arif, A. M.; Benac, B. L.; Cowley, A. H.; Jones, R. A.; Kidd, K. B.; Nunn, C. M. *New J. Chem.* **1988**, *12*, 553.

(21) Gabe, E. J.; Le Page, Y.; Charland, J. P.; Lee, R. L.; White, P. S. *J. Appl. Cryst.* **1989**, 22, 384.

Table 1. Crystallographic Data and Measurements^a for
 $\text{Et}_2\text{AlP}(\text{SiMe}_3)_2\text{Al}(\text{Et})_2\text{As}(\text{SiMe}_3)_2$ (1)

molecular formula	$\text{C}_{20}\text{H}_{56}\text{Al}_2\text{AsPSi}_4$
formula weight	568.87
crystal system	monoclinic
space group	$C2/c$ (C_{2h}^6)
a , Å	17.960(4)
b , Å	9.328(1)
c , Å	20.194(5)
β , deg	100.33(2)
V , Å ³	3328 (1)
Z	4
D_{calcd} , Mgm^{-3}	1.135
μ , mm^{-1}	1.266
temp, °C	-130
crystal dimens, mm	0.40 x 0.40 x 0.35
$T_{\text{max}}:T_{\text{min}}$	0.706:0.613
scan type	ω -2 θ
θ_{max} , deg	50
Total no of refls recorded	3028
no of non-equiv refls	2909
R_{merge} , on I	0.058
no of refls retained, $I > 2.5\sigma(I)$	2178

Table 1. Continued

no of parameters refined	128
R, R_w^b	0.030 (0.037)
goodness-of-fit ^c	1.19
max shift/ σ ratio; esd in final least-squares cycle	0.001
final $\Delta\rho(\text{e}/\text{\AA}^3)$ max;min	0.54;-0.23

^a Crystallographic calculations were performed on a DEC 3000/400 computer using the NRCVAX suite of structure determination programs.²¹ ^b $R = \sum|F_o| - |F_c|/\sum|F_o|$; $R_w = [\sum w (|F_o| - |F_c|)^2/\sum w |F_o|^2]^{1/2}$; $\sum w \Delta^2 [w = 1/\sigma^2(|F_o|)]$, $\Delta = (|F_o| - |F_c|)$ was minimized. ^c Goodness-of-fit = $[\sum w \Delta^2 / (N_{\text{observations}} - N_{\text{parameters}})]^{1/2}$.

Table 2. Non-Hydrogen Atom Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 1, with Estimated Standard Deviations in Parentheses

atom	x	y	z	$B_{eq}(\text{\AA}^2)$
As/P	0.81190(2)	0.25627(4)	0.07800(2)	1.36(2)
Al(1)	0.68036(4)	0.16600(8)	0.03872(4)	1.62(3)
Si(1)	0.89269(4)	0.07306(8)	0.12009(3)	1.98(3)
Si(2)	0.82685(4)	0.43877(8)	0.15610(4)	2.03(3)
C(1)	0.6022(2)	0.2699(3)	0.0771(1)	2.0(1)
C(2)	0.6015(2)	0.2363(3)	0.1509(2)	2.9(1)
C(3)	0.6764(2)	-0.0455(3)	0.0466(1)	2.2(1)
C(4)	0.5979(2)	-0.1044(4)	0.0452(2)	4.2(2)
C(11)	0.9900(1)	0.1449(4)	0.1453(2)	3.6(2)
C(12)	0.8920(2)	-0.0652(3)	0.0538(2)	3.1(1)
C(13)	0.8617(2)	-0.0130(3)	0.1939(2)	3.3(1)
C(21)	0.8262(2)	0.3654(3)	0.2418(1)	2.9(1)
C(22)	0.9179(2)	0.5338(4)	0.1561(2)	3.6(2)
C(23)	0.7474(2)	0.5676(3)	0.1340(2)	3.2(1)

Table 3. Selected Bond Distances (Å) and Angles (deg) for 1, with Estimated Standard Deviations in Parentheses

Bond Lengths			
As/P—Al(1)	2.499(1)	Si(1)—C(12)	1.857(3)
As/P—Al(1a)	2.494(1)	Si(1)—C(13)	1.863(3)
As/P—Si(1)	2.304(1)	Si(2)—C(21)	1.863(3)
As/P—Si(2)	2.303(1)	Si(2)—C(22)	1.860(3)
Al(1)—C(1)	1.974(3)	Si(2)—C(23)	1.857(3)
Al(1)—C(3)	1.981(3)	C(1)—C(2)	1.525(4)
Si(1)—C(11)	1.856(3)	C(3)—C(4)	1.510(4)
Bond Angles			
Al(1)—As/P—Al(1a)	90.44(3)	As/P(1a)—Al(1)—C(1)	113.08(9)
Al(1)—As/P—Si(1)	111.35(3)	As/P(1a)—Al(1)—C(3)	111.96(9)
Al(1)—As/P—Si(2)	116.99(3)	C(1)—Al(1)—C(3)	114.8(1)
Al(1a)—As/P—Si(1)	115.23(3)	As/P—Si(1)—C(11)	109.5(1)
Al(1a)—As/P—Si(2)	114.38(3)	As/P—Si(1)—C(12)	109.1(1)
Si(1)—As/P—Si(2)	107.90(3)	As/P—Si(1)—C(13)	110.9(1)
As/P—Al(1)—As/P	89.56(3)	As/P—Si(2)—C(21)	110.2(1)
As/P—Si(2)—C(22)	110.3(1)	As/P—Si(2)—C(22)	110.3(1)
As/P—Al(1)—C(1)	114.06(8)	As/P—Si(2)—C(23)	108.9(1)
As/P—Al(1)—C(3)	110.81(9)		

Captions to Figures

Figure 1. ORTEP diagram (30% probability ellipsoids) showing the solid state structure of $\text{Et}_2\text{AlP}(\text{SiMe}_3)_2\text{Al}(\text{Et})_2\text{As}(\text{SiMe}_3)_3$ (1). Hydrogen atoms have been omitted for clarity. Labeled and unlabelled atoms are related by a crystallographic 2-fold axis of symmetry.

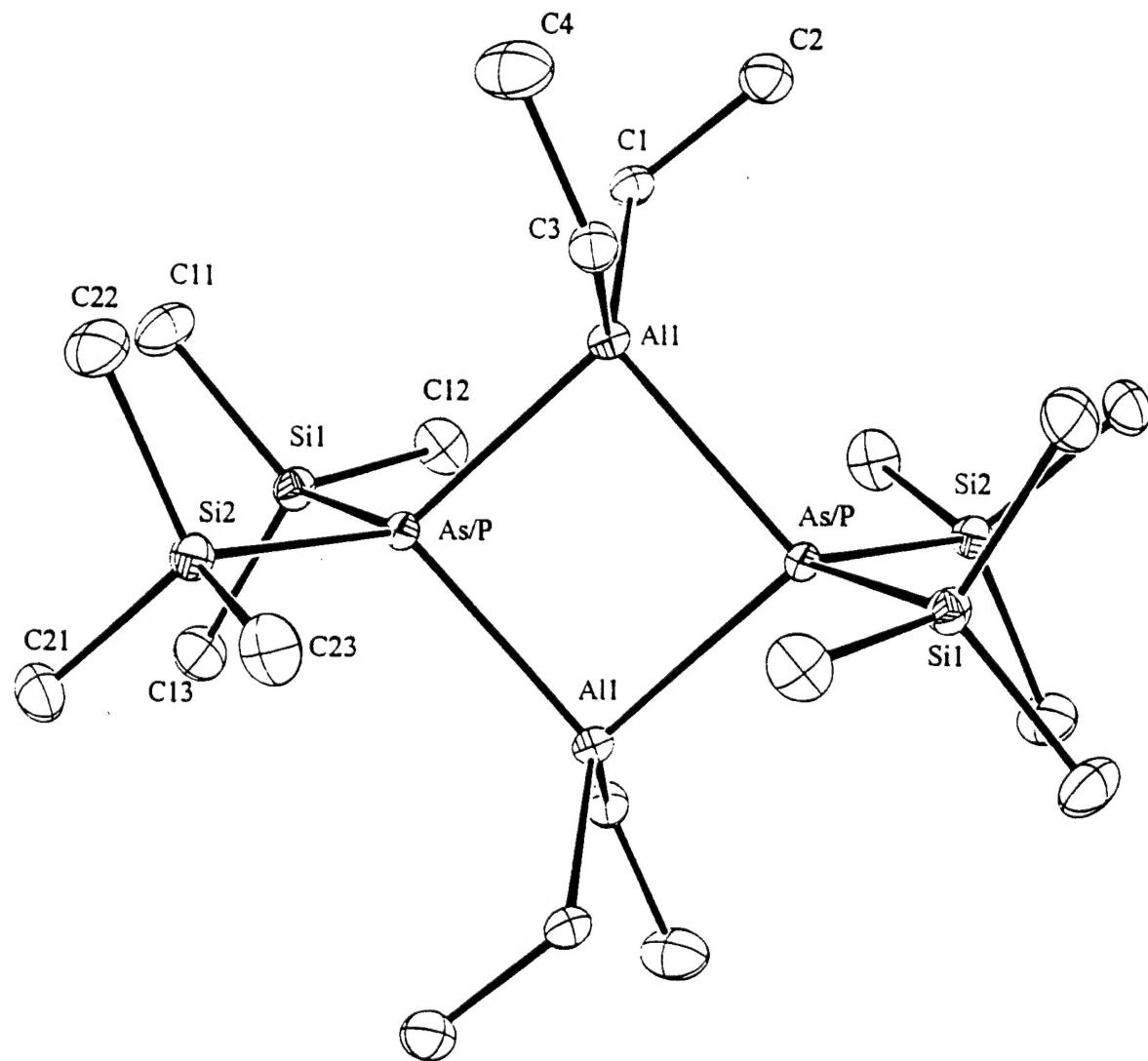


Figure 1